

Solid-State Esterification via Ionic-to-Covalent Bond Transformation in Ionic Molecular Crystals Consisting of Disubstituted Anthracene Anion-Cation Combinations

Masato Suzuki,^{*1} Takahiro Fujii,¹ Yoko Naito,¹ Kazuhisa Yamoto,¹ Shin-ichi Matsuoka,¹ Koji Takagi,¹ Haruki Sugiyama,² and Hidehiro Uekusa²

¹Department of Life Science and Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya, Aichi 466-8555, Japan

²Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan

E-mail: suzuki.masahito@nitech.ac.jp

Received: November 2, 2017; Accepted: December 7, 2017; Web Released: December 19, 2017



Masato Suzuki

Masato Suzuki was offered an assistant professor position at Kyoto University in 1985 before completing his Ph.D. He received his Ph.D. Degree from Kyoto University in 1988. He moved to Tokyo Institute of Technology as Associate Professor in 1994 and was promoted to Professor at Nagoya Institute of Technology in 2005. His major interest is polymer synthesis.

Abstract

Thermal solid-state reactions involving ionic-to-covalent bond transformation were achieved in the ionic molecular crystals of 1,8-bis[(pyridin-1-ium-1-yl)methyl]anthracene anthracene-1,8-dicarboxylate to produce the cyclic diester. The crystal structure given by X-ray diffraction analysis showed that the electrostatic interaction between the benzyl pyridinium cation and the carboxylate anion successfully works to locate these reaction sites close to each other and that there are channels for crystalline solvents and the liberated pyridine to escape. Thereby, the cyclic diester was selectively formed by the crystal-to-crystal reaction, which was proven by powder XRD profiles and optical microscopic and SEM images of the crystals before and after the reaction. This is the first thermal crystal-to-crystal condensation reaction. Another ionic molecular crystal of 1,8-bis[(pyridin-1-ium-1-yl)methyl]anthracene anthraquinone-1,8-dicarboxylate was also studied. Therein, the corresponding cyclic diester was also obtained, but the crystals were transformed to amorphous solid by the reaction.

1. Introduction

Solid-state reactions^{1,2} are attractive from the viewpoint of green chemistry. In addition, they are more fruitful when they involve characteristic production and specificity that are impossible to achieve in solution or melt reactions. The most characteristic features are presented by topochemical solid-state reactions,^{1–3} which proceed via single-crystal-to-single-crystal

transformations under crystal lattice control. However, topochemical reactions are almost exclusively promoted by light irradiation and strictly limited in number because they require special molecular arrangements in the crystals of the starting materials to minimize the molecular motion during the reaction.

With a view to control the structures and alignments of the product polymers, in which the molecular arrangements of the monomer crystals are fixed by the polymerizations, we have been focusing on solid-state thermal polycondensations,^{4,5} which are widely applicable to various substrates. In this context, we designed ionic crystals consisting of multi anion and cation combinations which undergo ionic-to-covalent transformation in the solid-state. Therein, the electrostatic interaction between the anion and the cation is expected to take an effective role in locating the reaction sites close to each other in the crystal. The elemental reaction we actually designed is the thermal transformation of benzylpyridinium carboxylate to benzyl ester along with the liberation of pyridine. Our recent article deals with the solid-state polycondensation on the basis of this strategy.⁵ Therein, the crystalline combination of two tetraphenylporphyrin derivatives, each of which has four benzylpyridinium cations and four carboxylate anions, respectively, produces the ladder polymer in the solid state. The molecular arrangement in the ionic crystal of the monomer governs the polymer linkage and alignment. We are expanding the scope of this strategy and in this article describe a thermal solid-state reaction of the combination of a 1,8-disubstituted anthracene dianion and dication derivative to produce the cyclic diester instead of the linear polymer and its analyses by TG-DTA, X-ray diffraction, optical and electron microscopy, as well as NMR and IR spectroscopy.

2. Experimental

The NMR spectra were recorded on Measurements. Bruker AVANCE III HD (400 MHz for ¹H) or AVANCE 500US CryoProbe (500 MHz for ¹H) spectrometers in CDCl₃, CDCl₃ with CF₃CO₂H, DMSO-d₆, CD₃OD, or D₂O. Chemical shift values in ¹HNMR spectra are relative to the internal TMS standard in CDCl₃, the signal due to the residual protons of DMSO-d₆ (2.50 ppm) or CD₃OD (3.31 ppm), or the internal sodium 3-trimethylsilyl-1-propanesulfonate standard in D₂O. Chemical shift values in ¹³C NMR spectra are relative to CDCl₃, CD₃S(=O)CD₃, or CD₃OD resonance (77.00, 39.52, and 49.00 ppm, respectively), or the internal sodium 3-trimethylsilyl-1-propanesulfonate standard in D₂O. The IR spectra were recorded on a FT/IR-460 Plus spectrometer by an ATR method. Electrospray ionization mass spectrometry (ESI-MS) was performed on a Waters Synapt G2 HDMS tandem quadrupole orthogonal acceleration time-of-flight instrument. Thermogravimetry and differential thermal analyses (TG-DTA) were performed with a Simadzu DTG-60 apparatus (heating rate: 10 °C/min, under a N2 flow). Powder X-ray diffraction was measured on a glass plate at r.t. by a Rigaku SmartLab system equipped with a CuKa X-ray source and a D/teX Ultra detector. Single crystal X-ray diffraction was measured by a Rigaku VariMax RAPID-II system. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1573951. Copies of the data can be obtained free of charge via CCDC Website. Optical microscopy was performed using a OLYMPUS BX50 apparatus with a combination of eye (10X) and object (50X) lenses. Samples for SEM were prepared by Au-atomic coating under vacuum and viewed with electron beam of 10 KV acceleration voltage at 1000- and 5000-fold magnifications by a JEOL JSAM-6010LA apparatus.

Synthesis of 1,8-Dicyanoanthraquinone. The procedure in a previous report⁶ was modified. A mixture of 1,8dichloroanthraquinone (10.0 g, 34.4 mmol) and CuCN (12.4 g, 138 mmol) in dry DMAc (80 mL) was refluxed overnight and then poured into water (300 mL). The precipitate underwent suction filtration to give a dark-green solid, which was successively washed with aqueous NH₃ solution (5 wt%, 500 mL) and water. The obtained grey solid was suspended into 3M HNO₃ (350 mL) and heated at 60 °C for 4 hr. The mixture cooled to r.t. was filtered, washed with water and MeOH, and dried under vacuum to give 1,8-dicyanoanthraquinone as a grey solid (9.25 g). ¹H NMR (400 MHz, DMSO- d_6): δ (ppm) 8.49 (dd, J = 7.9, 1.2 Hz, 2H), 8.41 (dd, J = 7.8, 1.2 Hz, 2H), 8.10 (t, J = 7.8 Hz, 2H). IR (cm⁻¹): 2226 (vC \equiv N), 1676 (vC=O).

Synthesis of Anthraquinone-1,8-dicarboxylic acid. The acidic hydrolysis of 1,8-dicyanoanthraquinone gave anthraquinone-1,8-dicarboxylic acid,⁶ which was further purified as follows when it was used for the anionic component of **3**. Anthraquinone-1,8-dicarboxylic acid (0.524 g, 1.77 mmol) was dissolved into an NaOH (166 mg, 4.14 mmol) aqueous solution. Vapor diffusion recrystallization with acetone gave reddish black needle-like crystals, which were collected by

decantation, washed with acetone, and dissolved into water again. Acidification with conc. HCl afforded milky brown solid, which was collected by filtration, washed with H₂O, and dried under vacuum to recover anthraquinone-1,8-dicarboxylic acid (0.326 g, 1.10 mmol, 62%). ¹H NMR (400 MHz, DMSO-d₆,): δ (ppm) 8.28 (dd, J = 7.8, 1.1 Hz, 2H), 7.96 (t, J = 7.6 Hz, 2H), 7.84 (dd, J = 7.5, 1.1 Hz, 2H). IR (cm⁻¹): 1703 (vC=O), 1670 (vC=O).

Synthesis of Anthracene-1,8-dicarboxylic acid. The procedure in the previous report⁶ was modified. Anthraquinone-1,8-dicarboxylic acid (1.00 g, 3.38 mmol), Zn dust (3.79 g, 58.0 mmol), and aqueous NH₃ solution (20 wt%, 44 mL) were refluxed at 80 °C for 5 hr. Water (33 mL) was added, and the mixture was stirred for 1 hr at r.t. The insoluble part was removed by filtration and washed with water. The combined filtrate was acidified with conc. HCl, and the precipitate was collected by suction filtration and dried at 50 °C under vacuum to give anthracene-1,8-dicarboxylic acid as yellowish green solid (0.520 g, 1.95 mmol, 58%). In order to use it for the anionic component of 1, further purification was performed as follows. Anthracene-1,8-dicarboxylic acid (0.298 g, 1.12 mmol) was dissolved into an aqueous solution of NaOH (98.8 mg, 2.47 mmol). The solution was filtered and subjected to recrystallization by a vapor diffusion of acetone. The dark brown precipitate was collected by filtration, washed with acetone, and then dissolved into water. Acidification with conc. HCl formed yellow solid, which was collected by filtration, washed with H₂O, and dried in vacuo to give anthracene-1,8-dicarboxylic acid (0.183 g, 0.686 mmol, 61%). ¹H NMR (400 MHz, DMSO d_6): δ (ppm) 10.46 (s, 1H), 8.78 (s, 1H), 8.34 (d, J = 8.6 Hz, 2H), 8.19 (dd, J = 6.9, 1.0 Hz), 7.62 (dd, J = 6.9, 8.6 Hz, 2H).

Synthesis of 1,8-Bis(hydroxymethyl)anthracene. To a dry THF (10 ml) solution of anthracene-1,8-dicarboxylic acid (1.81 g, 6.80 mmol) under ice cooling was slowly added 1 M BH₃ solution in THF (27 mL, 27 mmol). Overnight stirring at r.t. was followed by the careful addition of water (70 mL) under ice cooling. Brine was added to the reaction mixture, which was then extracted with five portions of EtOAc. When the EtOAc-insoluble part was observed, it was collected by suction filtration and suspended in aqueous 2 M NaOH solution. Then, the insoluble solid, which was 1,8-bis(hydroxymethyl)anthracene, was re-collected by filtration, washed with water, and dried under vacuum. On the other hand, the EtOAc-extracted portion was dried over MgSO₄, concentrated, and subjected to recrystallization with EtOAc-acetone or to silica gel column chromatography (EtOAc, $R_f = 0.50$). Totally, 1,8-bis(hydroxymethyl)anthracene was obtained in 49% yield (0.791 g, 3.32 mmol,) as yellowish green solid, which was used for the next step without further purification. ¹H NMR (400 MHz, DMSOd₆): δ (ppm) 8.74 (s, 1H), 8.59 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 7.0 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 5.47 (t, J = 5.4 H, 2H), 5.12 (d, J = 5.4 Hz, 4H).

Synthesis of 1,8-Bis(bromomethyl)anthracene. PBr₃ (2.22 g, 8.20 mmol) was added dropwise to 1,8-bis(hydroxymethyl)anthracene (791 mg, 3.32 mmol) in CH₂Cl₂ (30 ml) under ice cooling. The reaction mixture stirred at r.t. overnight was diluted with CHCl₃ and washed with NaHCO₃ aq. three times. The organic layer was dried over MgSO₄ and vacuumdried to give 1,8-bis(bromomethyl)anthracene (0.919 g, 2.52 mmol, 76%) as yellow solid, which was used for the next step without further purification. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.01 (s, 1H), 8.54 (s, 1H), 8.04 (d, J = 8.6 Hz, 2H), 7.63 (d, J = 6.8 Hz, 2H), 7.43 (dd, J = 6.8, 8.6 Hz, 2H), 5.16 (s, 4H).

Synthesis of 1,8-Bis[(pyridin-1-ium-1-yl)methyl]anthracene dibromide. A mixture of 1,8-bis(bromomethyl)anthracene (919 mg, 2.52 mmol) and pyridine (4 mL) was stirred at r.t. for 4 hr. MeOH was added to give a homogenous solution, which was then added dropwise into Et₂O. The yellow solid precipitated was collected by centrifugation and dissolved into MeOH again. The solution was filtered through a Teflon membrane (pore size 0.45 µm) and subjected to vapour diffusion recrystallization using MeOH with Et₂O. The obtained solid was washed with Et₂O and dried under vacuum to give yellow solid of 1.8-bis[(pvridin-1-ium-1-vl)methvl]anthracene dibromide (914 mg, 1.75 mml, 69%). ¹H NMR (400 MHz, CD₃OD): δ (ppm) 9.07 (d, J = 6.0 Hz, 4H), 8.84 (s, 1H), 8.70 (s, 1H), 8.64 (t, J = 7.7 Hz, 2H), 8.29 (d, J = 8.6 Hz, 2H), 8.12 (dd, J = 6.8, 7.7 Hz, 4H), 7.63 (dd, J = 6.8, 8.6 Hz, 2H), 7.50 (d, J = 6.8 Hz, 2H), 6.63 (s, 4H).

Synthesis of 1,8-Bis[(pyridin-1-ium-1-yl)methyl]anthracene anthracene-1,8-dicarboxylate (1). There are two preparation ways as follows.

a) Anthracene-1,8-dicarboxylic acid (51.9 mg, 0.194 mmol) and 1,8-bis[(pyridin-1-ium-1-yl)methyl]anthracene dibromide (100 mg, 0.191 mmol) was stirred with Ag₂O (50.4 mg, 0.217 mmol) in MeOH (30 mL) at r.t. overnight. The mixture was centrifuged, and the supernatant was vacuum-dried and dissolved again into MeOH/H₂O (2/1 v/v, 3 mL). The solution was filtered through a Teflon membrane (pore size 0.45 µm) and subjected to vapour diffusion recrystallization with acetone under dark conditions to form yellow needle-like crystals, which were washed with acetone and vacuum-dried to afford 1 (65 mg) containing 4.5 wt% (evaluated by TGA) of MeOH/H₂O, thus, in 51% yield.

b) An aqueous solution (40%) of tetrabutylammonium hydroxide (360 mg, 0.555 mmol) was added to anthracene-1,8dicarboxylic acid (74.7 mg, 0.281 mmol) in MeOH (1 mL). To the mixture stirred for 10 min was added 1.8-bis[(pyridin-1ium-1-yl)methyl]anthracene dibromide (145 mg, 0.277 mmol). After 2 hr with stirring at r.t., the mixture was added dropwise to Et₂O to give a milky brown precipitate, which was collected by centrifugation and vacuum-died. The obtained crude product of 1 (166 mg, 0.264 mmol) was purified by vapour diffusion recrystallization as mentioned above. ¹HNMR spectrum (400 MHz, CD₃OD): δ (ppm) 9.94 (s, 1H), 9.15 (s, 1H), 9.01 (d, J = 5.6 Hz, 4H), 8.68 (s, 1H), 8.37 (t, J = 7.8 Hz, 2H), 8.28 (s, 1H), 8.14 (d, J = 8.7 Hz, 2H), 7.87 (m, 6H), 7.65 (dd, J = 6.8, 1.0 Hz, 2H), 7.48 (dd, J = 6.9, 8.7 Hz, 4H), 7.41 (dd, J = 6.8, 8.5 Hz, 2H), 7.08 (d, J = 6.9 Hz, 2H), 6.85 (s, 4H). ¹³C NMR spectrum (100 MHz, CD₃OD): δ (ppm) 177.6, 146.6, 146.3, 140.9, 133.4, 133.0, 132.2, 131.4, 130.6, 130.1, 130.0, 129.6, 129.2, 128.1, 127.7, 126.4, 126.0, 125.8, 125.6, 118.6, 63.4. NMR spectra are shown in Figures S1-S4 in Supporting Information.

Synthesis of 1,8-Bis[(pyridin-1-ium-1-yl)methyl]anthracene anthraquinone-1,8-dicarboxylate (3). To an aqueous solution (0.5 mL) of anthraquinone-1,8-dicarboxylic acid (29.5 mg, 0.100 mmol) were successively added solutions of tetrabutylammonium hydroxide in H_2O (40%, 130 mg, 0.200 mmol)



Figure 1. Thermal solid-state reaction.

and of 1,8-bis[(pyridin-1-ium-1-yl)methyl]anthracene dibromide (52.0 mg, 0.100 mmol) in H₂O (1 mL). After 1 hr with stirring, dropwise addition of the mixture into Et₂O afforded a precipitate, which was collected by centrifugation and washed with Et₂O. The brown solid obtained was reprecipitated from MeOH solution into Et₂O twice and vacuum-dried to give 3 (49.0 mg, 0.075 mmol) as milky brown solid. Vapour diffusion recrystallization from MeOH-H2O solution with acetone under dark conditions was repeated twice to form red crystals along with dark brown powder, the former of which were picked up by using tweezers (27.4 mg, 0.042 mmol, 42%). ¹H NMR spectrum (400 MHz, D₂O): δ (ppm) 8.69 (d, J = 5.8 Hz, 4H), 8.48 (t, J = 7.6 Hz, 2H), 8.10 (s, 1H), 7.94 (t, J = 7.1 Hz, 4H), 7.72(d, J = 8.6 Hz, 2H), 7.56 (s, 1H), 7.32 (m, 2H), 7.21 (m, 4H),7.15 (t, J = 7.7 Hz, 2H), 7.02 (d, J = 6.7 Hz, 2H), 6.04 (s, 4H). 13 C NMR spectrum (D₂O, 100 MHz): δ (ppm) 183.3, 182.6, 177.5, 146.1, 144.1, 141.0, 133.7, 131.6, 131.5, 131.0, 130.7, 129.7, 129.7, 128.3, 128.2, 127.5, 126.8, 125.4, 125.3, 114.9, 61.6. NMR spectra are shown in Figures S5–S8 in Supporting Information.

General Procedure for Thermal Solid-State Reaction. Crystals of 1 or 3 were heated on a glass plate under N₂ flow by using an aluminium block bath (Figure 1). The spectroscopic data for product 2 are shown by Figures 4, 5, and S9–S12. TG-DTA showed that the decomposition of 2 started at 313 °C without melting. The spectroscopic data for product 4 are shown by Figures S14 and S17–S21. ESI MS: Found 499.1181 ($C_{32}H_{18}O_6$ +H), 521.0999 ($C_{32}H_{18}O_6$ +Na); Calc 499.1176 ($C_{32}H_{18}O_6$ +H), 521.1001 ($C_{32}H_{18}O_6$ +Na). Mp. 350 °C (dec.).

3. Results and Discussion

1,8-Bis[(pyridin-1-ium-1-yl)methyl]-Preparation of anthracene anthracene-1,8-dicarboxylate (1). The anionic component, anthracene-1,8-dicarboxylic acid, was prepared by the reported procedure⁶ and transformed to the cationic component, 1,8-bis[(pyridin-1-ium-1-yl)methyl]anthracene dibromide (Scheme 1). They were combined to give 1 by the counter anion exchange of the benzylpyridinium salt from bromide to carboxylate, mediated by silver(I) oxide or tetrabutylammonium hydroxide. The former reagent works to precipitate AgBr, and the pyridinium carboxylate is isolated from the supernatant. The latter reagent converts the carboxylic acid to the tetrabutylammonium carboxylate, which is subjected to ionexchange with the pyridinium bromide. The pyridinium carboxylate is separated from the tetrabutylammonium bromide by reprecipitation into Et₂O. The ionic combination compound, 1, was prepared in this manner and purified by vapour diffusion recrystallization under dark conditions.

Crystal Structure of 1.⁷ Pale yellow needle-like crystals of **1** were obtained by the vapour diffusion method from a MeOH-



Scheme 1. Preparation of ionic molecular combination 1.

H₂O solution with acetone. The MeOH and H₂O included in the crystal were found to escape quite easily, leading the crystal to crack and diminishing the data quality from X-ray crystallography. However, quickly mounting the crystal gave satisfactory analytical data. Figure 2 shows the graphical views of the molecular arrangements in the crystal of 1. The crystalline solvents of H₂O and MeOH occupy a channel-like region in the crystal, and they can easily escape through these channels (Figures 2a-c). The anionic and cationic atoms, i.e., the carboxyl oxygen (red) and the pyridinium benzyl carbon (blue), are located closely to each other, and show a weak interaction between them (Figure 2d). This electrostatic interaction is assisted by the CH- π and π - π stacking interactions to pair the cationic and anionic molecules. As mentioned in the Introduction, the pyridine-liberating condensation would take place between the carboxylate oxygen anion and the pyridinium benzyl carbon atom. The distances between them are 3.22-3.51 Å (Figure 2e), which are smaller than the Schmidt rule distances, 3.6-4.2 Å, defined for the reaction sites in the phototopochemical cycloadditions of C=C bonds.³ The molecular arrangement of 1 in the crystal suggests the predominant transformation to the cyclic diester by thermal condensation.

Thermal Reaction of 1. As seen in a typical TG-DTA profile of **1** (Figure 3), increasing temperature leads to a small weight decrease due to vaporization of the included solvents and a subsequent sharp weight decrease corresponding to the endothermic peak ascribable to the chemical reaction liberating pyridine. This is supported by good agreement of the observed weight loss (23.4%) with the calculated value (25.2%). The onset temperature for the reaction was sensitively affected by the purity and the solvent composition in the crystal and was observed between 175-230 °C.

Since an excessively high reaction temperature is usually unfavorable in terms of side reactions, the thermal reaction was examined at 180 °C on a glass plate under N₂ and dark conditions, even for the sample that showed the onset reaction temperature of 230 °C. Thereby, IR spectroscopy showed the vC=O and vC-O absorption bands of the ester appearing at 1701 and 1257 cm⁻¹, respectively, and simultaneously the v_{as}CO₂⁻ and v_sCO₂⁻ absorption bands of the carboxylate anion disappearing at 1562 and 1363 cm⁻¹, respectively (Figure 4).



Figure 2. X-ray analysed crystal structures of **1** (crystalline solvents such as MeOH and H₂O are omitted): a)–c) one-layer views from three directions along crystal axes, where the interrupted line ellipses show the areas including the solvents, d) interactions between the components, and e) distances between the reaction sites.



Figure 3. TG-DTA profiles of 1.

The reaction mixture obtained by heating **1** at $180 \,^{\circ}$ C for 2 days was dissolved in CDCl₃ with CF₃CO₂H (TFA) and analysed by ¹H NMR spectroscopy which revealed that cyclic diester **2** was quantitatively produced (Scheme 2, Figure 5). There are two



Figure 4. IR spectra before and after heating (180 °C, 2 days) of 1.



Scheme 2. Thermal reaction of 1 to 2.



Figure 5. ¹H NMR spectra (400 MHz, CDCl₃/TFA (8/2 v/v)) of the reaction mixture obtained by heating **1** at 180 °C for 2 days: δ (ppm) 9.97 (s, 1 H), 9.29 (s, 1 H), 8.54 (s, 1 H), 8.40 (s, 1 H), 8.16 (dd, *J* = 7.1, 1.0 Hz, 2 H), 8.09 (dd, *J* = 8.4, 5.0 Hz, 4 H), 7.83 (dd, *J* = 6.6, 1.0 Hz, 2 H), 7.45–7.56 (m, 4 H), 6.70 (d, *J* = 11.7 Hz, 2 H), and 6.04 (d, *J* = 12.0 Hz, 2 H).

doublet peaks at 6.04 and 6.70 ppm with J = 12 Hz, characteristic of geminal coupling of benzylic methylene protons, suggesting the cyclic structure. It is noteworthy that 2 dissolved in CDCl₃ with TFA underwent some hydrolysis within 12 hr. Additional NMR and ESI-MS spectroscopy (Figures S10–S12) supported the identification of 2. Alternatively, 2 was also quantitatively obtained by heating 1 to 300 °C at a rate of 10 °C/min in a TG-DTA apparatus.⁸

Figure 6 shows the XRD profiles of 1 and the reaction mixtures. Profile (b) was obtained for 1 that was crushed by sonication in acetone and subjected to measurement with soaking in acetone. Therein, the peak patterns in the low-angle area showed similarity to profile (a) that was given by calculating the single crystal structure of Figure 2. Then, drying 1 under air and vacuum led these peaks to shift to larger angle area (profiles (c) and (d)). These observations suggest that the large



Figure 6. XRD profiles of 1 and the reaction mixtures: (a) the pattern calculated from the crystal structure of Figure 1, (b) 1 soaked with acetone, (c) 1 dried under air, (d) 1 dried under vacuum, (e) the reaction mixture at 75% conversion of 1, (f) the reaction mixture at almost 100% conversion of 1, and (g) the reaction mixture dissolved into CHCl₃ with TFA and then immediately dried.



Figure 7. Optical microscopic views before and after heating of 1, without (upper photos) and with (lower photos) a pair of cross polarizers.

scale molecular arrangement in crystals of 1 employed for the reaction is consistent with the graphic views in Figure 2 and undergoes shrinking of the crystal lattices by loss of the crystalline solvents by way of heating. At 75% conversion, which was evaluated from the weight decrease, there were new peaks observed together with those due to 1 which disappeared at 100% conversion (profiles (e) and (f)). Since there is a possibility that the crystals formed by the reaction may have a difference in molecular arrangement from the usual crystal of 2, we measured the XRD profile of the crystals of 2 (profile g). Therein, the reaction mixture of profile (f) was once dissolved into CHCl₃ with TFA and immediately dried under vacuum to give the crystals of 2. Consequently, profile (f) was found almost identical to profile (g). Thus, these findings along with the microscopic observation (vide infra) prove that the thermal ionic-to-covalent bond transformation from 1 to 2 is a crystalto-crystal reaction even though release of pyridine is involved. According to a literature survey, there is such a reaction; however, it is a crystal-to-crystal photoreaction with N₂ release.⁹

Optical microscopy apparently proved that the reaction of 1 to 2 took place in the solid state (Figure 7). There was no melting process, showing a thin string-like morphology remained even after the reaction. However, during the progress of the reaction, a number of cracks appeared in the crystals



Figure 8. SEM images of 1 before and after heating.



Scheme 3. Thermal reaction of 3 to 4.

and the interference colouration was weakened, leading to the formation of very brittle and yellow ochre crystals. 10

Figure 8 shows SEM images of **1** and the reaction product. Since the samples were prepared by Au-atomic coating under vacuum, escape of the crystalline solvents from **1** formed cleavages probably along the c crystal axis. After the reaction, there was observed a regularly aligned belt-like texture. The granular particles on the surface are likely due to fracture of the brittle crystals.

Thermal reaction of 1,8-bis[(pyridin-1-ium-1-yl)methyl]anthracene anthraquinone-1,8-dicarboxylate (3). Anthraquinone-1,8-dicarboxylic acid, which is the precursor of the anionic component of 1, was employed to prepare another ionic compound, 3, consisting of the anthracene and anthraquinone combination. However, no single crystal of 3 for the X-ray analysis was obtained. The TG-DTA data revealed that the reaction started at 180 °C and the weight decrease (21%) was consistent with the theoretical value (24%) that was calculated for the esterification with liberation of pyridine (Figure S13). Thus, the thermal reaction of 3 was conducted on a glass plate at 160 °C for 4.5 h and subsequently at 170 °C for 7 h under N₂ (Scheme 3). The formation of the ester was suggested by the IR spectra (Figure S14). However, in contrast with the reaction of 1, disappearance of crystallinity was revealed by XRD as well as cross-polarized optical microscopy (Figures S15 and S16). The main part (86%) of the reaction mixture was CHCl₃ soluble, showing a single spot on TLC. NMR (Figures S17-21) and ESI mass spectra (see the Experimental) suggested that cyclic diester 4 was selectively produced also from 3 like 1.

4. Conclusion

The thermal crystal-to-crystal reaction has been achieved first time by ionic-to-covalent bond transformation even though it is a kind of condensation. The molecular packing in the ionic molecular crystal was found favorable to promote the crystalto-crystal reaction. The electrostatic interaction plays a strong role to locate the reaction sites, the electrophilic carbon and the carboxylate anion, close to each other. The distances between them are smaller than the Schmidt rule values defined in topochemical photoreactions. In addition, the crystal has channels for liberated pyridine to escape readily. These findings give us a clue to expand the scope of widely applicable solid-state reactions.

The authors are indebted to Prof. Kenji Nagata (Nagoya Institute of Technology) for obtaining the SEM images. This work was supported by JSPS KAKENHI Grant Number 21550117.

Supporting Information

NMR spectra of **1** and **3**. Additional spectroscopic data of **2**. The thermal reaction data for **3** (TG-DTA and XRD profiles, IR spectra, and optical microscopic views). NMR spectra of **4**. These materials are available on http://dx.doi.org/10.1246/bcsj. 20170349.

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7 Crystal data for 1 recrystallized from a MeOH/H₂O solution with acetone: C₄₂H₃₀N₂O₄•0.5(CH₄O)•7(H₂O), triclinic, *P*-1, *a* = 11.2673(8), *b* = 17.1540(9), *c* = 20.6764(13) Å, *α* = 91.946(3)°, *β* = 100.273(3)°, *γ* = 97.790(3)°, *V* = 3889.0(4) Å³, *Z* = 4, μ = 0.791 mm⁻¹, final R indices [I>2 σ (I)]: R₁ = 0.0996, wR₂ = 0.3105, CCDC 1573951.

8 The solution reaction was also performed; 1,8-bis[(pyridin-1-ium-1-yl)methyl]anthracene dibromide and anthraquinone-1,8-dicarboxylic acid were dissolved into dry DMSO with dry pyridine (20 eq.) and heated at 150 °C under N₂. The ¹HNMR spectra showed that a complex mixture was formed without **2**.

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